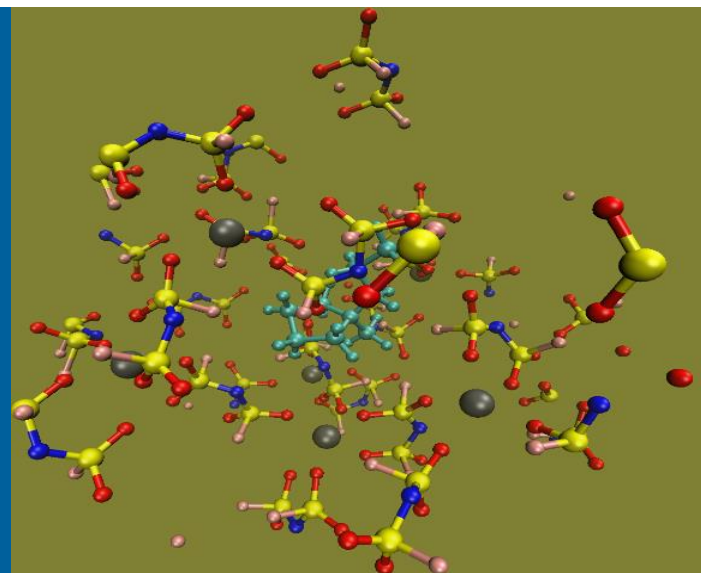


WE START WITH YES.

Stabilizing Cathode/Electrolyte Interphase by New Electrolyte Design



Zhengcheng (John) Zhang (P. I.)
Argonne National Laboratory

June 9-13, 2019

Project ID # BAT374

Overview

Timeline

- Project start: Oct. 1, 2018
- Project end: Sept. 30, 2021
- Percent complete: 33%

Budget

- Total project funding
 - 100% DOE funding
- Funding for FY 2019: \$350 K

Barriers

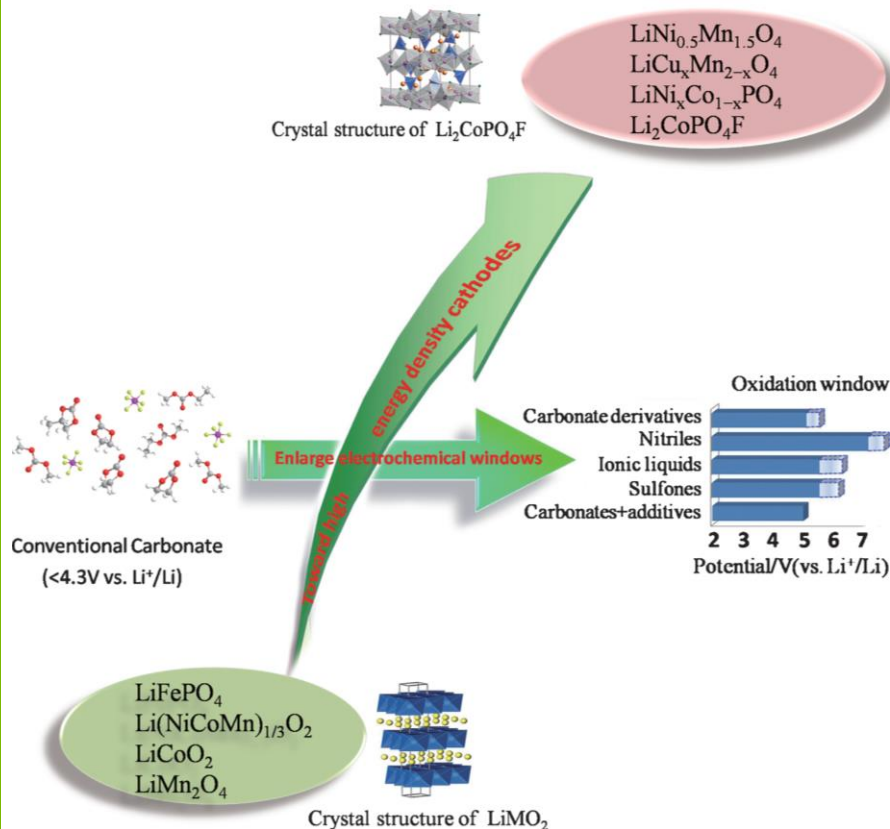
- Cycle and calendar life – Next generation batteries
- Thermodynamic stability at cathode/electrolyte interphase
- Abuse Tolerance

Partners

- PNNL
- NREL
- University of Illinois – Chicago (UIC)
- Northern Illinois University (NIU)
- Lydall Performance Materials (Netherlands)

- Project Lead: ANL

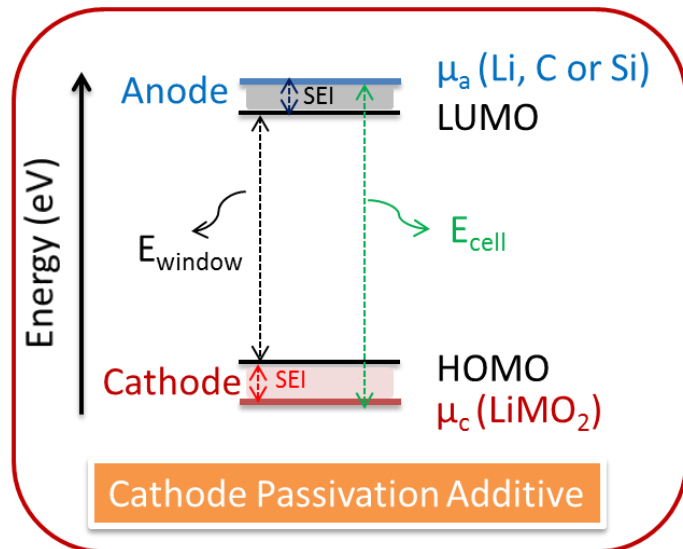
Relevance - Project Objectives



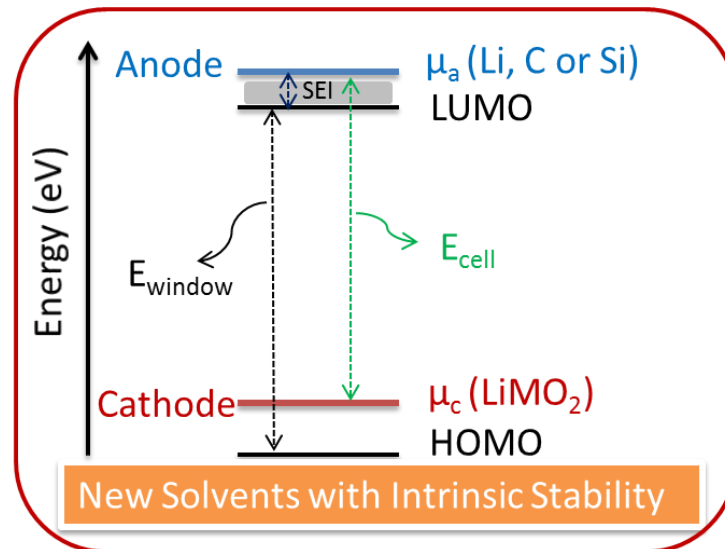
- ❑ Next-generation lithium-ion battery requires high-voltage high-energy density for long-range electric vehicle applications.
- ❑ Cathode materials with high voltage (> 4.3 V) and high capacity (>200 mAhg⁻¹) with low cost are greatly demanded.
- ❑ The performance of high-voltage high-energy cells are compromised due to the instable cathode/electrolyte interphase caused by the decomposition of electrolytes and transition metal dissolution-diffusion-deposition cycle.
- ❑ The objective of this project is to design and develop stable electrolyte materials that can thermodynamically stabilize the cathode/electrolyte interphase.
- ❑ The new electrolyte materials could tolerate high charging voltages (>5.0 V vs Li^+/Li) of the Ni-rich, low-Co cathodes and are compatible with other cell components.

Technical Approach and Strategy

Electrolyte Additives

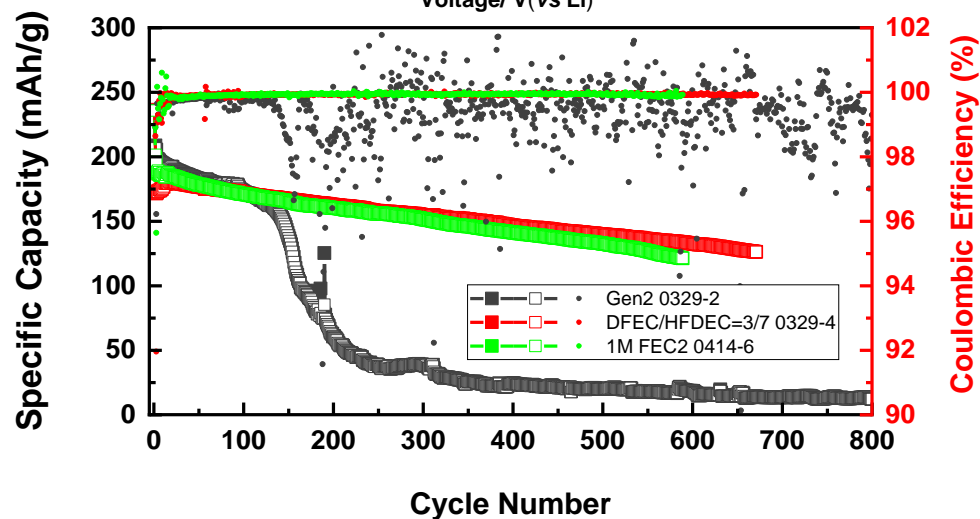
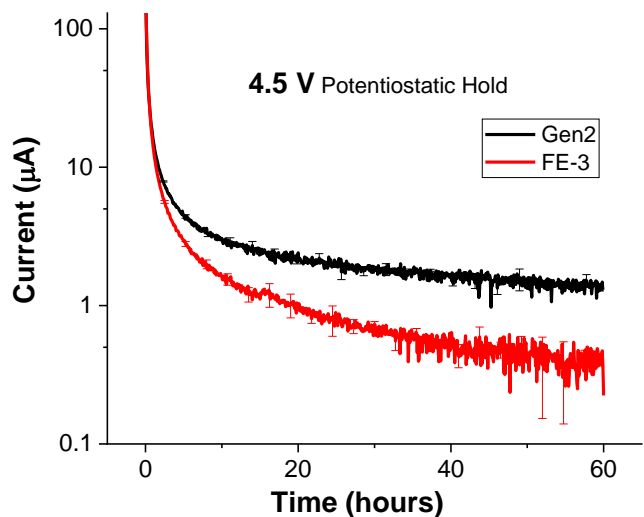
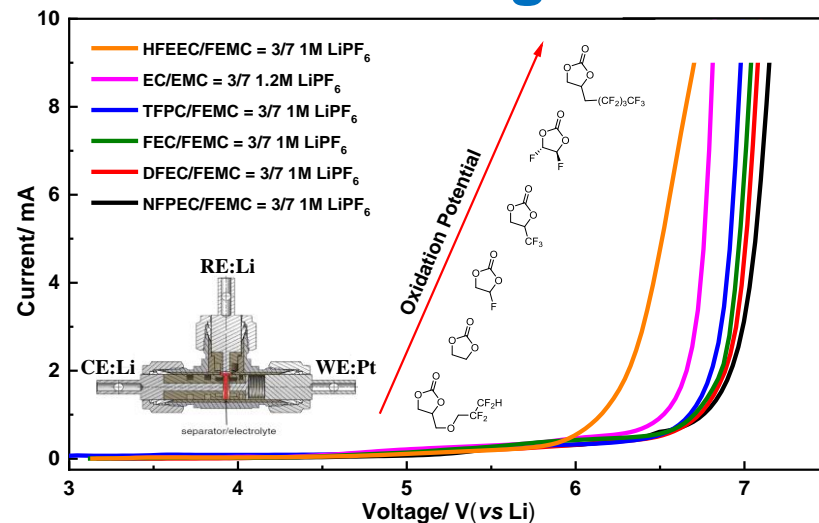
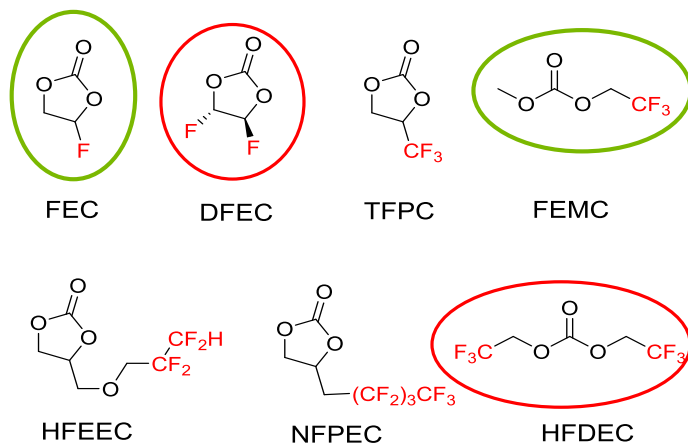


Electrolyte Solvents



- ✓ Molecular design of additives that could be oxidatively decomposed and deposited on the surface of cathode forming a cathode-electrolyte-interphase (CEI) to provide kinetic stabilization at the cathode/electrolyte interphase at high voltages.
- ✓ Design and develop new electrolyte solvents to provide thermodynamic stability at cathode/electrolyte interphase at high voltages. Incorporation of electron-withdrawing groups (fluorine and fluorinated alkyl) to the conventional solvents could lower the HOMO energy level, thus expand the electrochemical window up to 5.0 V vs Li⁺/Li.

Technic Accomplishments and Progress

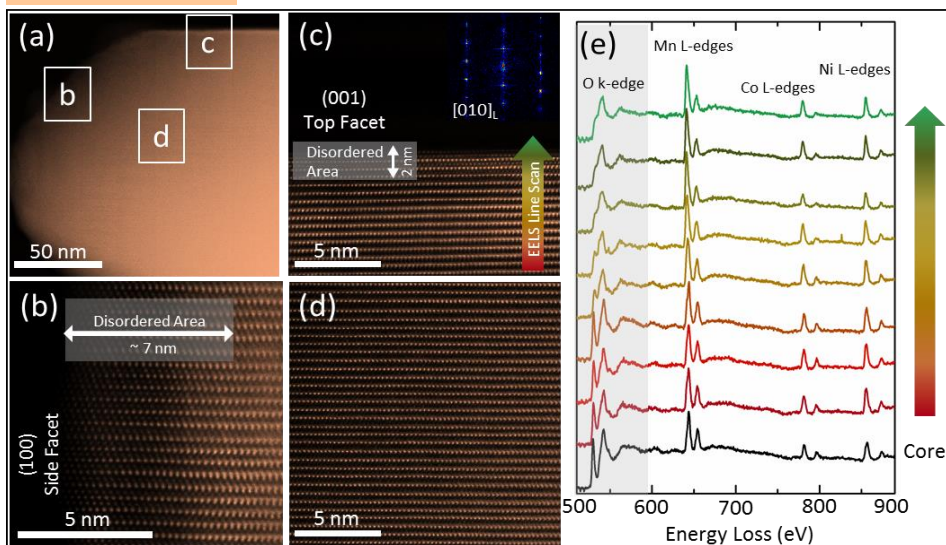


- The formulated FEC/F-EMC and DFEC/HFDEC electrolytes are stable at high voltage as evidenced by the results from linear sweep voltammetry (Pt/Li/Li cell) and potentiostatic-hold experiment (NMC532/graphite charged to 4.5 V and hold for 60 h).
- NMC532/graphite full cell cycling data (4.5-3.0 V, C/3) indicate both electrolytes not only stabilize the cathode surface at high charging voltages, but also are capable of forming the SEI via reductive decomposition on the graphite anode.

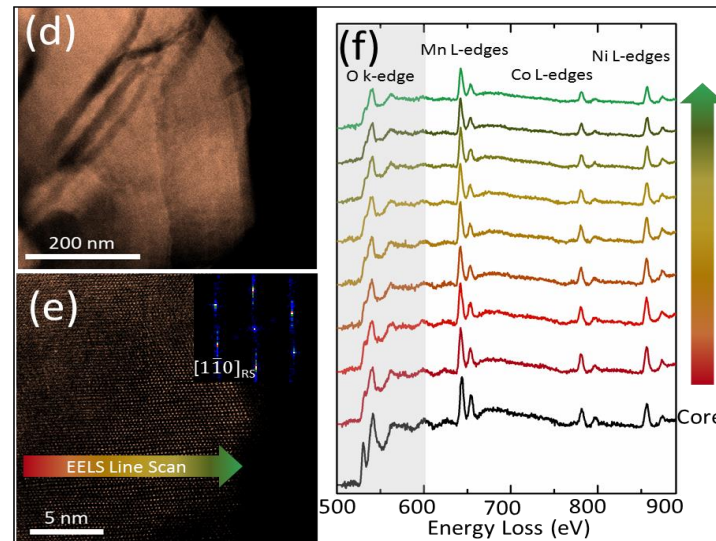
HRTEM/EELS and SEM Analysis of Cycled Electrodes

NMC532

Cycled in FE-3 electrolyte

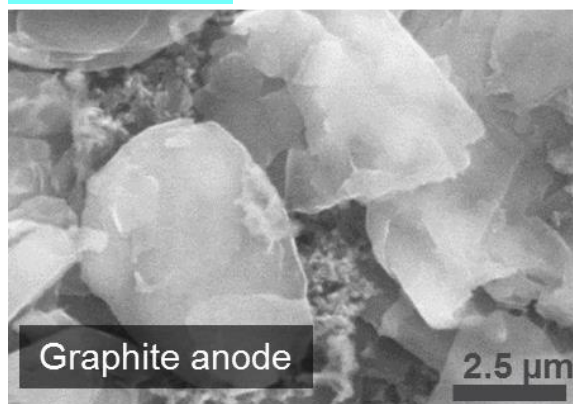


Cycled in Gen 2 electrolyte

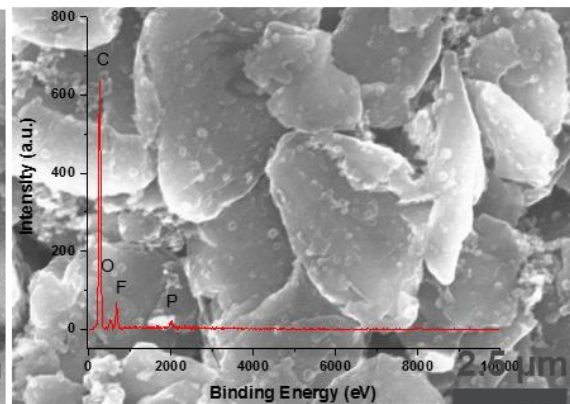


Graphite

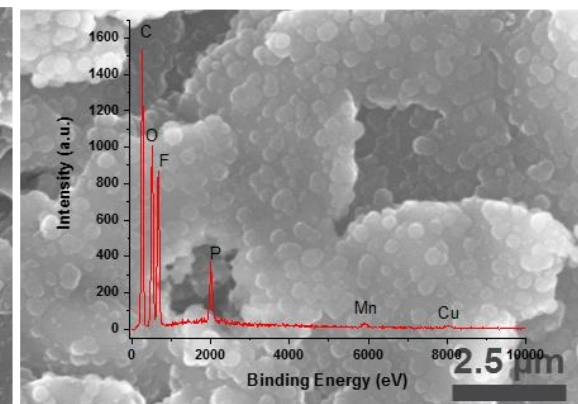
Pristine



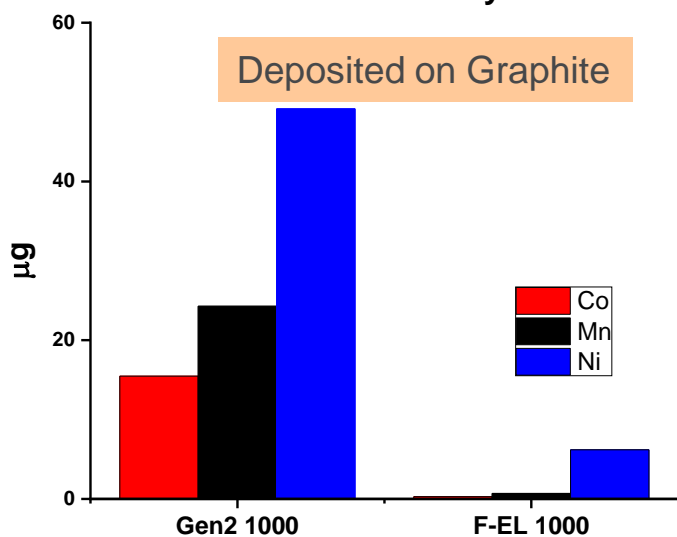
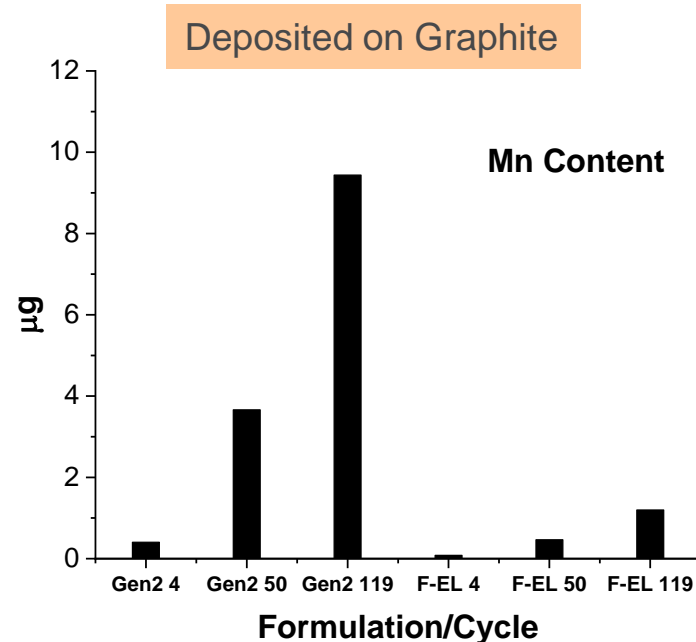
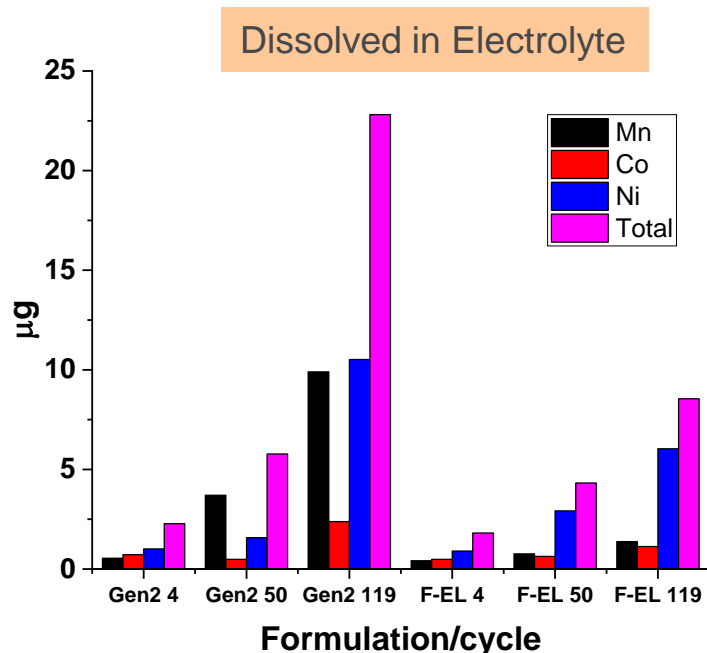
Cycled in FE-3 electrolyte



Cycled in Gen 2 electrolyte



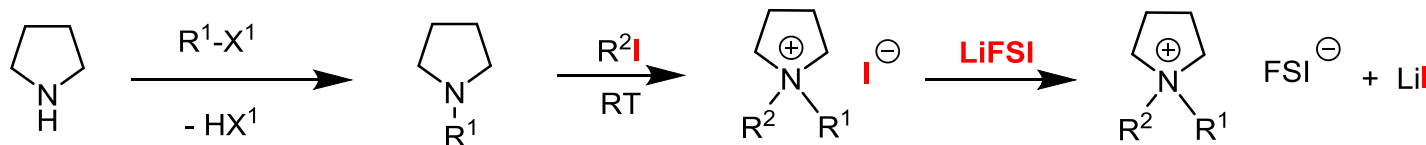
Quantify Transition Metal Dissolution by ICP-MS



- For all NMC532 samples, Ni most likely to leave the cathode.
- Vastly different Mn dissolution behavior with Gen 2 and fluorinated electrolyte F-EL.
 - ✓ Large amount of Mn dissolution (beyond stoichiometric composition)
 - ✓ Requires oxygen loss (no Mn^{3+} with normal battery operation)
- Co has similar electrolyte concentration but very low content deposited on the anode.
- Much more total TM measured in cycled Gen 2 electrolyte.

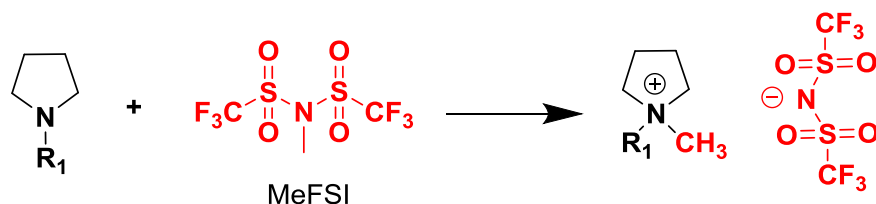
One-Step Synthesis of Ionic Liquids: High Purity, Low Cost

Traditional synthesis of IL:

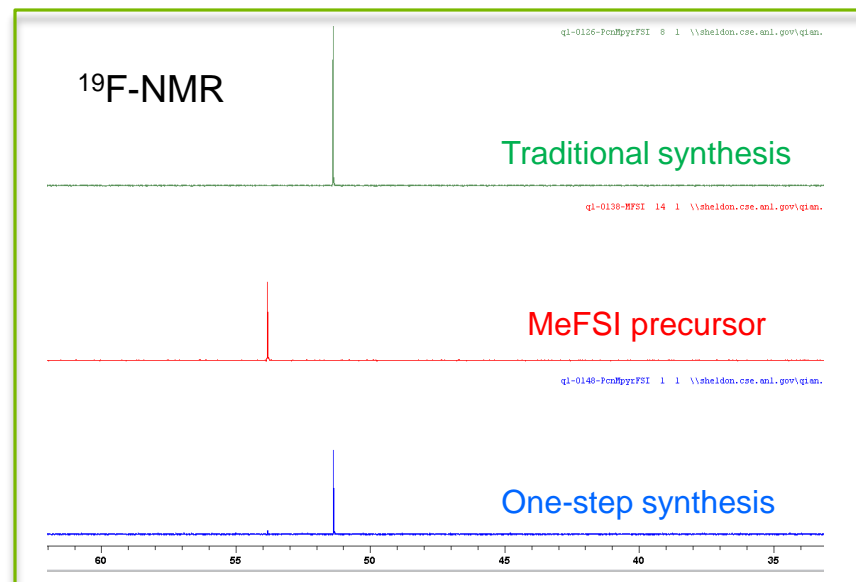
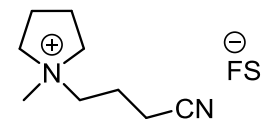


- Multiple steps, labor intensive
- Possible halide contamination
- Li salt availability and purity

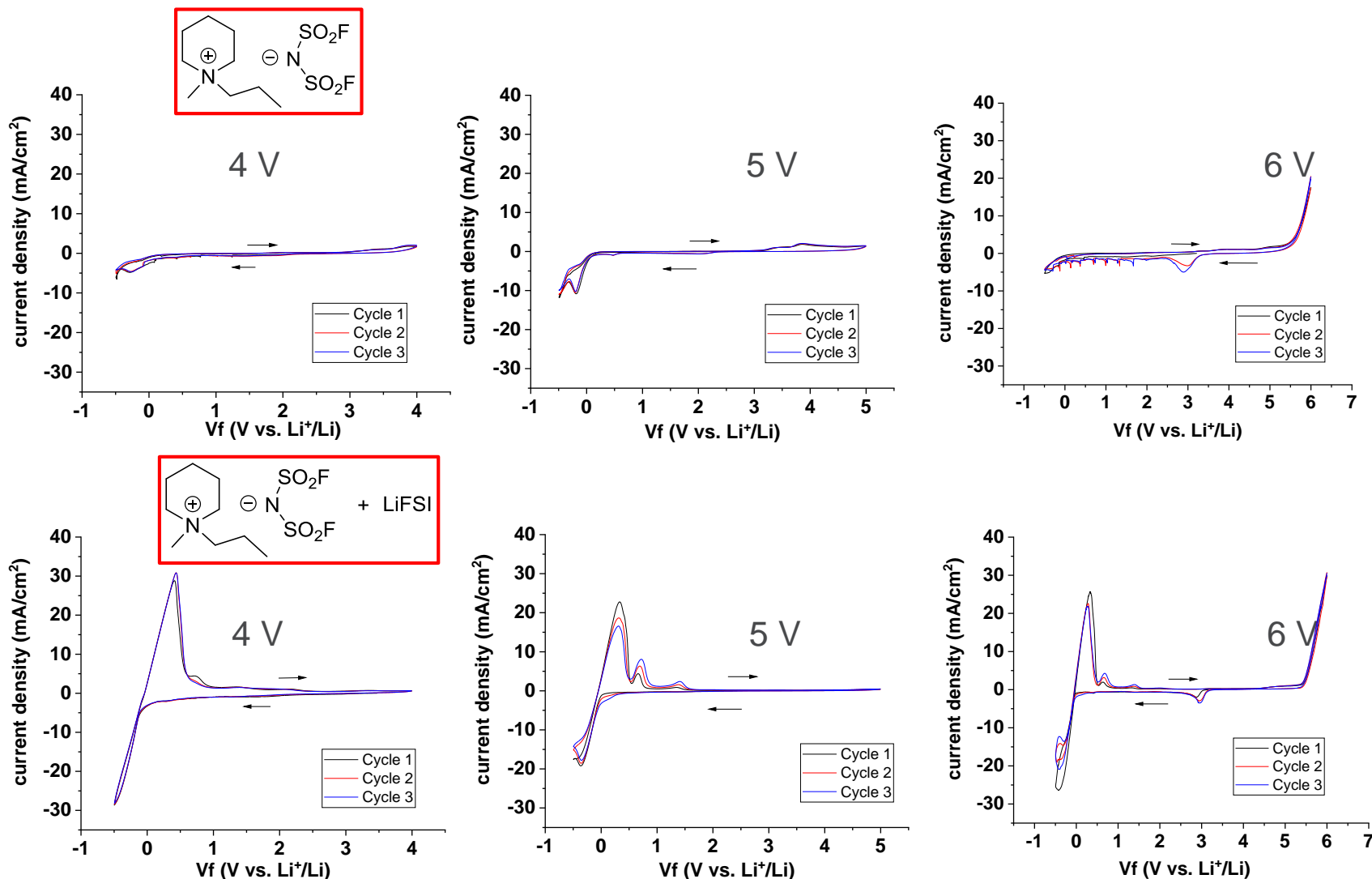
New synthesis of IL: Halide-free



- ✓ One step synthesis: green chemistry
- ✓ Halide-free synthesis
- ✓ Ultra-high purity starting material
- ✓ MERF: scale-up of MeFSI



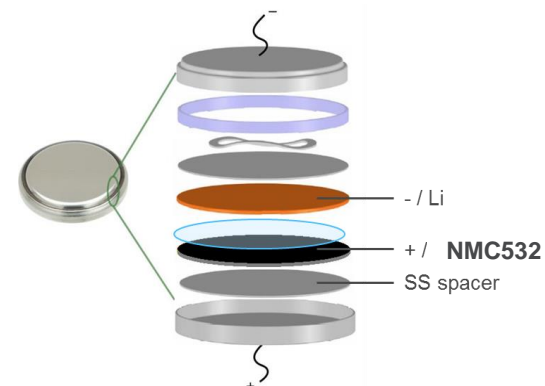
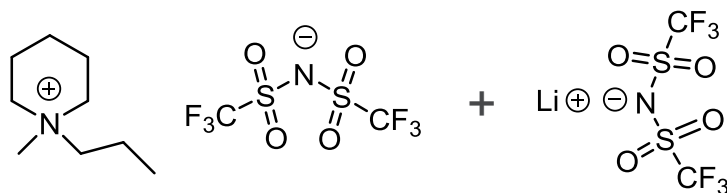
Voltage Stability of IL-Electrolyte: Cyclic Voltammetry



- ✓ CV data indicate both IL and IL-LiFSI electrolytes are stable up to 5.5 V vs Li⁺/Li, stable at the interface of most cathode materials with high-voltage and high-capacity.

LiFSI Concentration Impact on Cell Performance

PMpipFSI-LiFSI



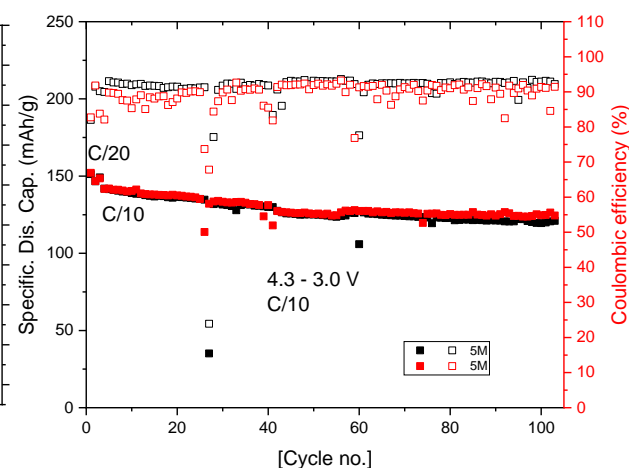
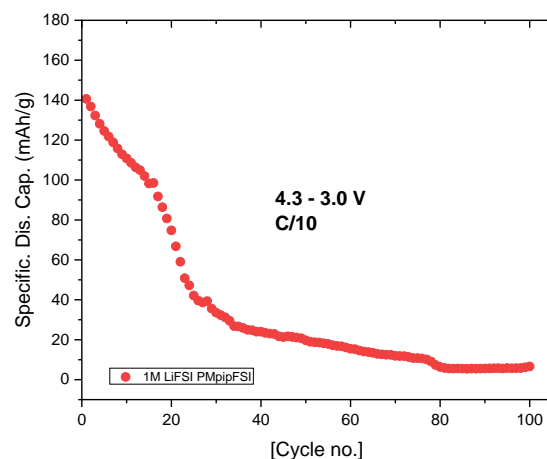
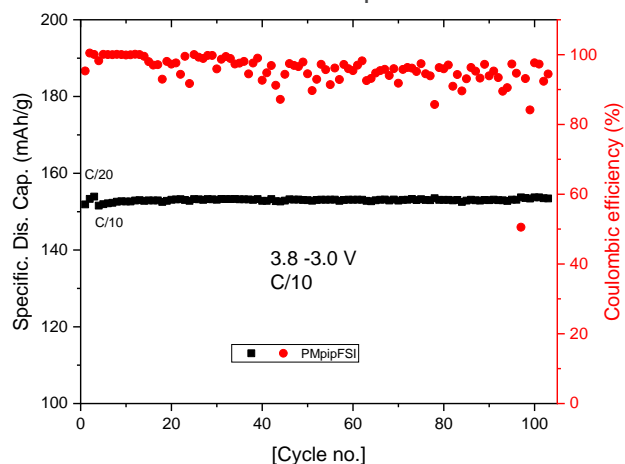
1 M LiFSI

5 M LiFSI

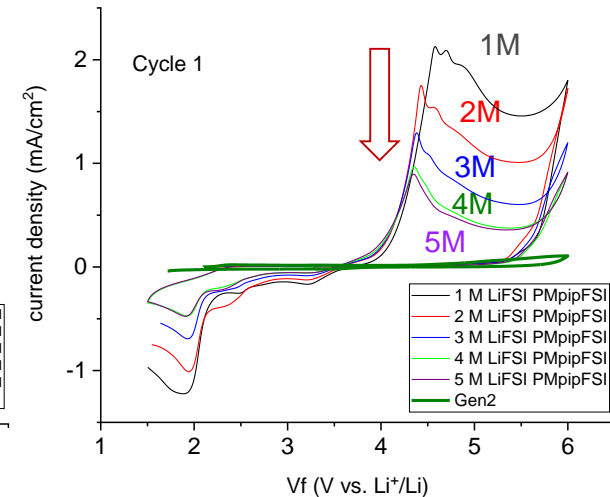
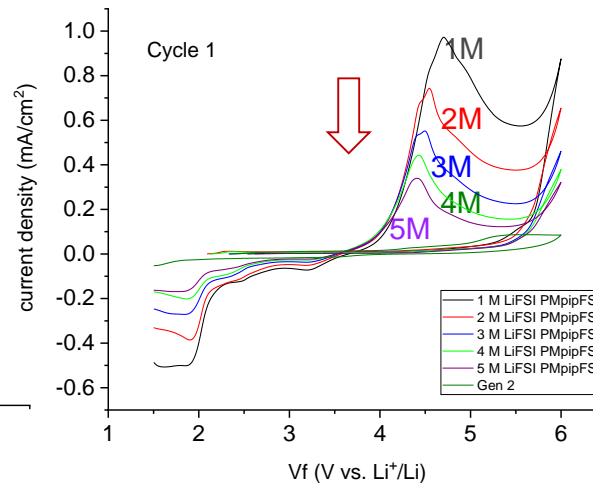
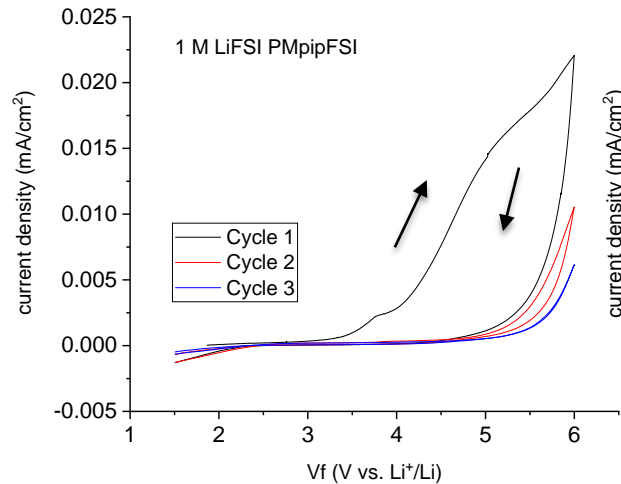
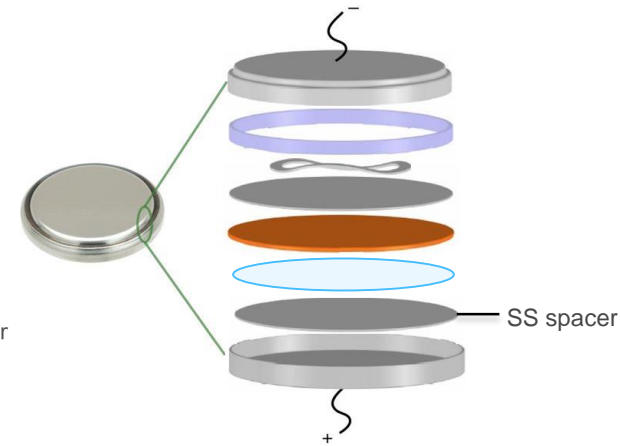
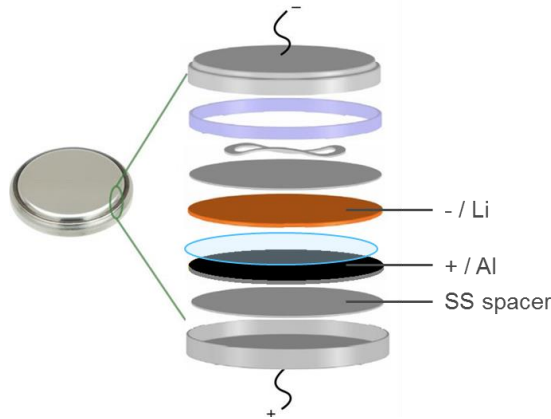
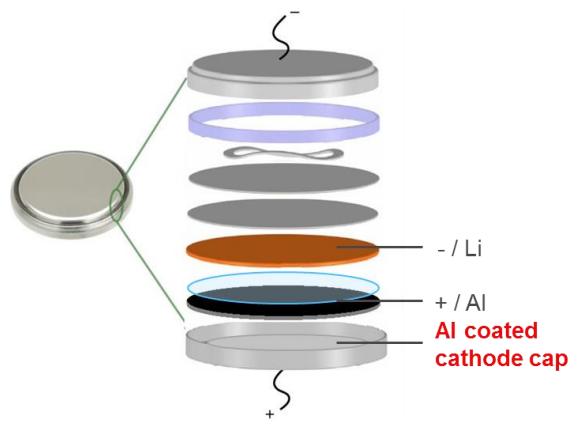
LiFePO₄/Li

LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂/Li

LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂/Li



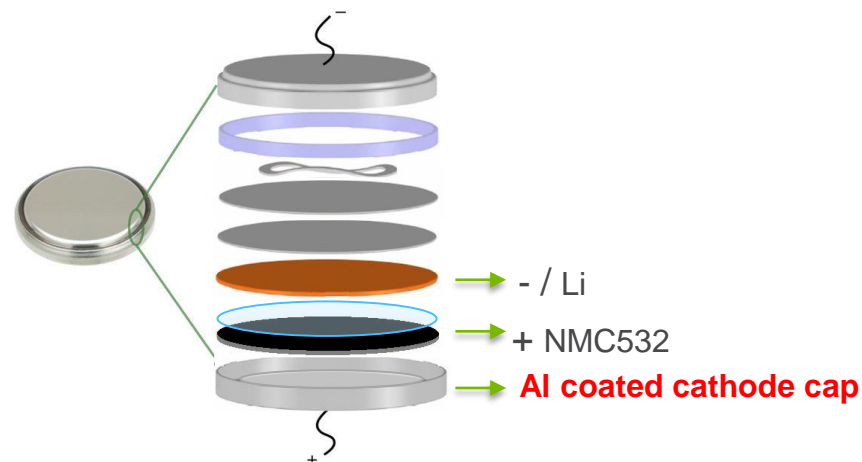
Stainless Steel (SS) Corrosion: Incompatibility Issue



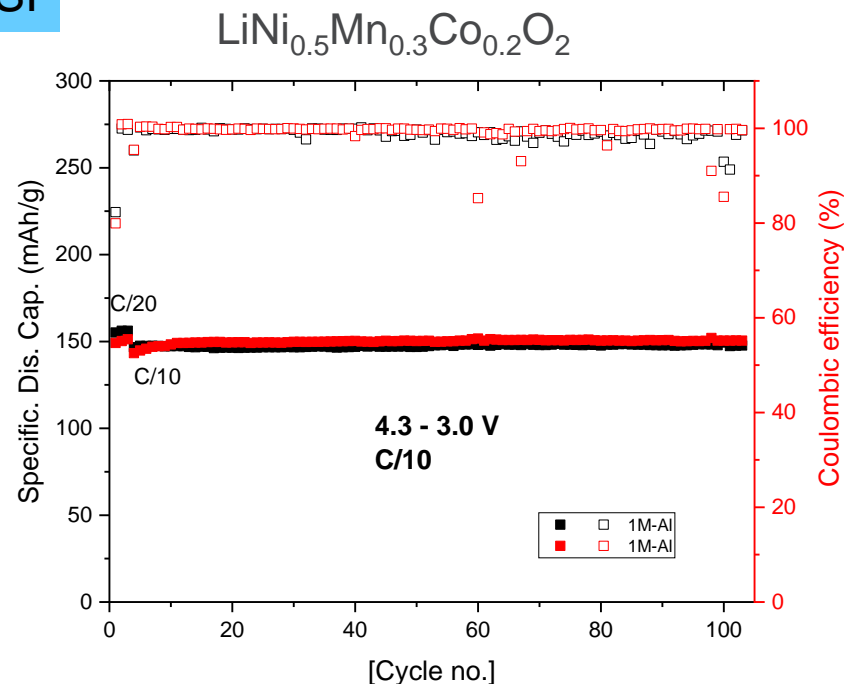
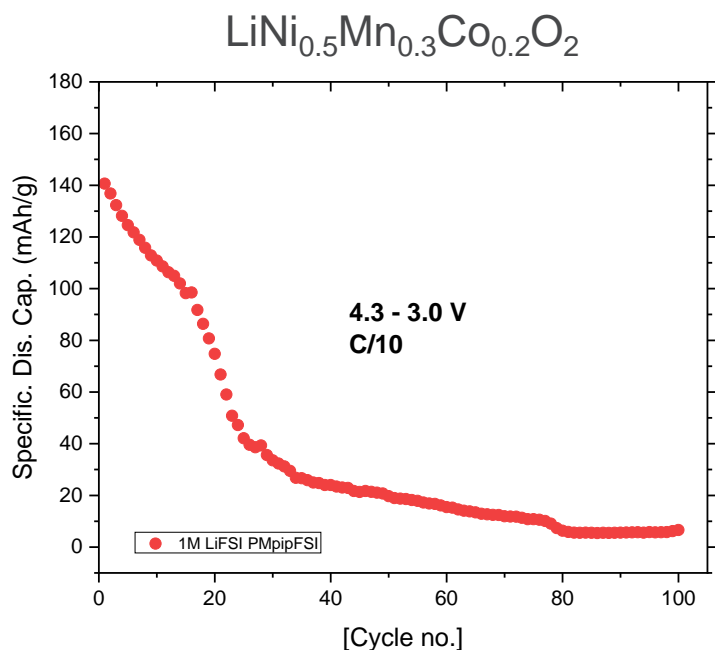
- All IL-electrolytes could passivate Al current collector, but severe corrosion was observed when stainless steel (SS) spacer is present in the coin cell.
- IL-electrolyte with high LiFSI concentrations could kinetically slow down the SS corrosion process, thus enable the normal cycling of NMC cells with regular cell configuration.

SS Corrosion-Free $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2/\text{Li}$ Cell Performance

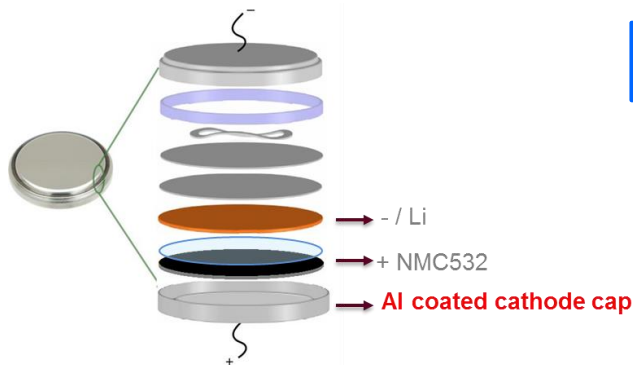
Coin cell parts: Al-coated
Cutoff voltage: 4.3-3.0 V
Cycling T = 30°C



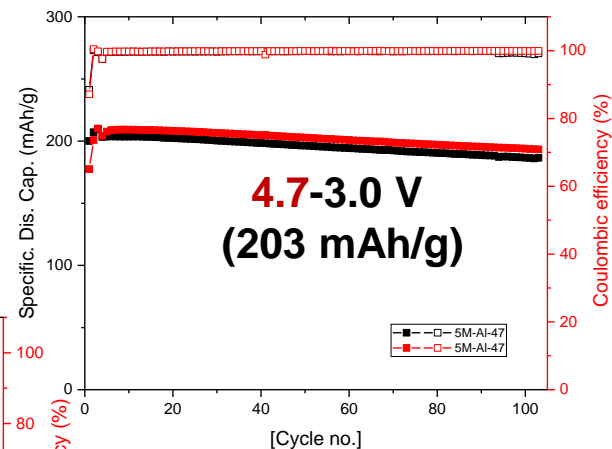
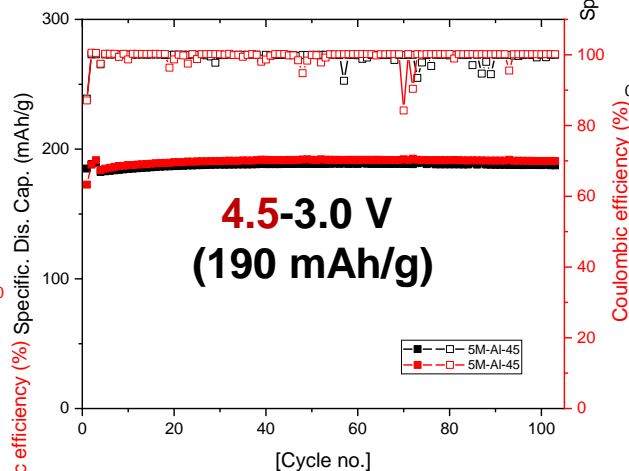
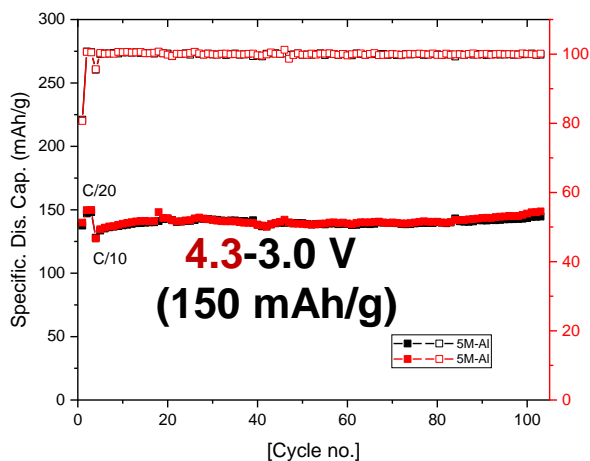
1 M LiFSI



Impact of High Salt Concentration on High Voltage Cells



5 M LiFSI in PM_{pip}FSI

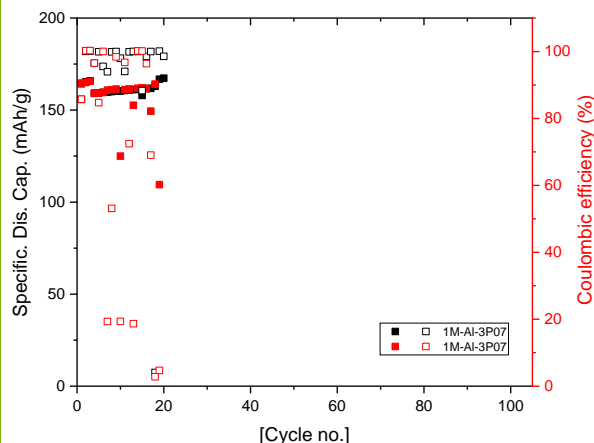


- ❑ 5 M LiFSI IL electrolyte showed exceptional capacity retention with close to 100% Coulombic efficiency.
- ❑ When cycled at 4.7 V, the NMC/Li half cells showed much improved high voltage performance than Gen 2.

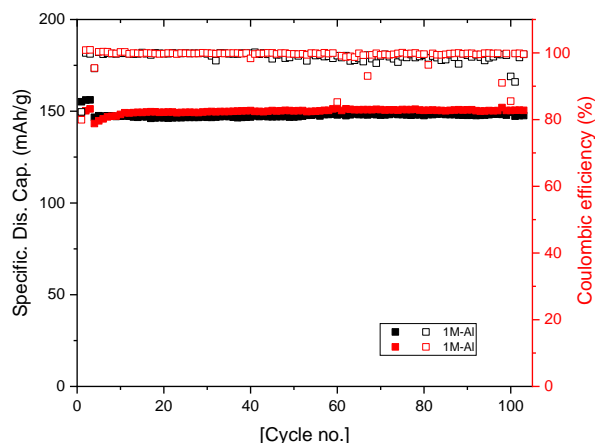
Wetting Issue with PP/PE/PP Separators

Separator	Pore Size (μm)	Porosity (%)	Thickness(μm)
Celgard 2325	0.028	39	25
Solupor 3P07	0.7	83	20
Whatman GF/F	0.7	100	420
Solupor 7P03	0.3	85	50

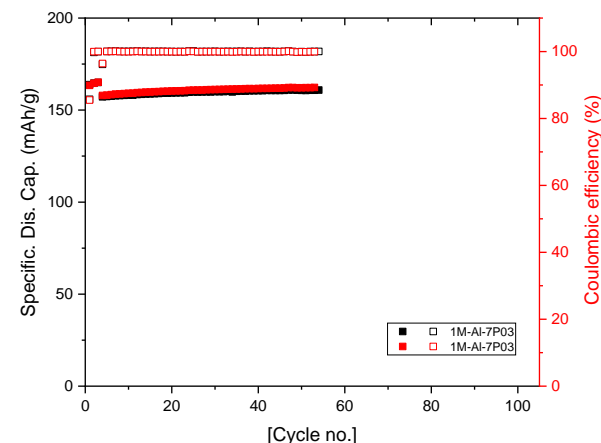
3P07



GF/F

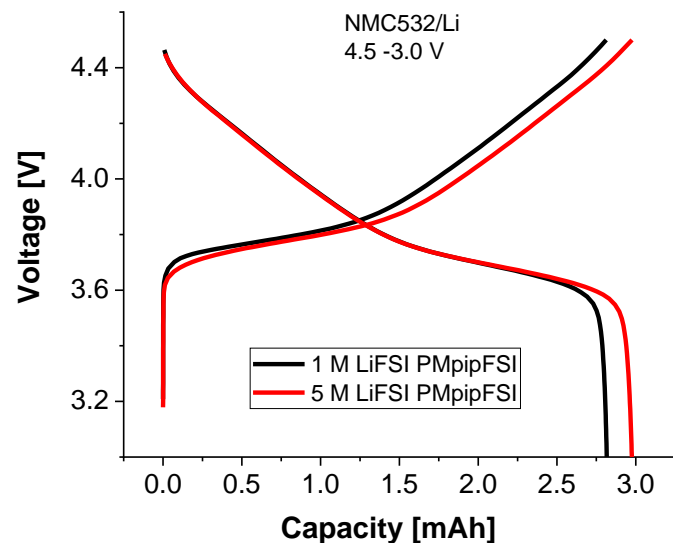
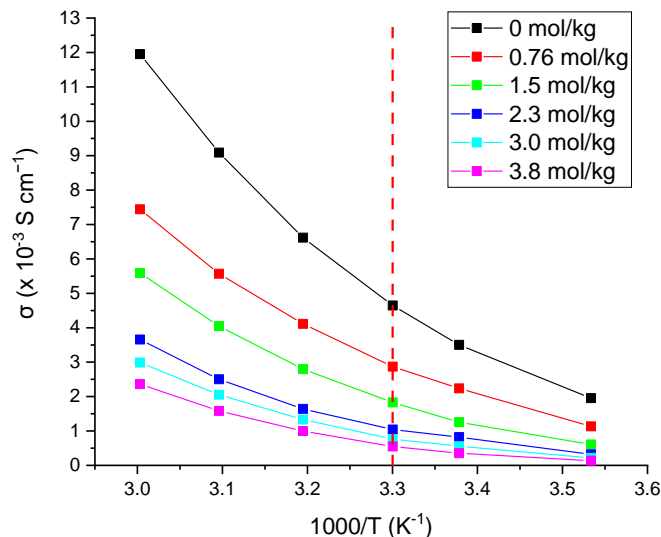


7P03



- ✓ IL-electrolytes (low and high salt concentrations) couldn't wet the hydrophobic polyolefin based separators.
- ✓ Glass-fiber and paper based separators are compatible with IL electrolytes with Solupor 7P03 shows the best cell performance.

Viscosity, Conductivity and Li⁺ Transference Number



[LiFSI] (mmol)	Molality of LiFSI (mol/kg)	Mole ratio of each ion			Viscosity cP	Conductivity S/cm @ RT	Li ⁺ transference number
		Li ⁺	PMpip ⁺	FSI ⁻			
0	0	0	0.50	0.50	87.25	3.50	
1	0.76	0.10	0.40	0.50	133.5	2.24	0.164
2	1.5	0.16	0.34	0.50	249.0	1.25	0.185
3	2.3	0.21	0.29	0.50	396.0	0.819	0.340
4	3.0	0.25	0.25	0.50	601.3	0.555	0.344
5	3.8	0.28	0.22	0.50	936.6	0.353	0.475

- ✓ High t_{Li^+} for highly concentrated IL-electrolyte facilitates the Li⁺ transfer in the electrolyte bulk.
- ✓ Although six times higher viscosity, 5 M IL electrolyte showed slightly low voltage polarization and delivered a slightly higher capacity.

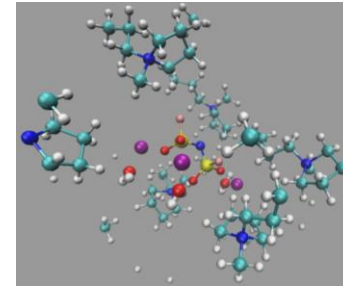
Conductivity Enhancement for Improved C-Rate

5 M LiFSI PMpipFSI Electrolyte

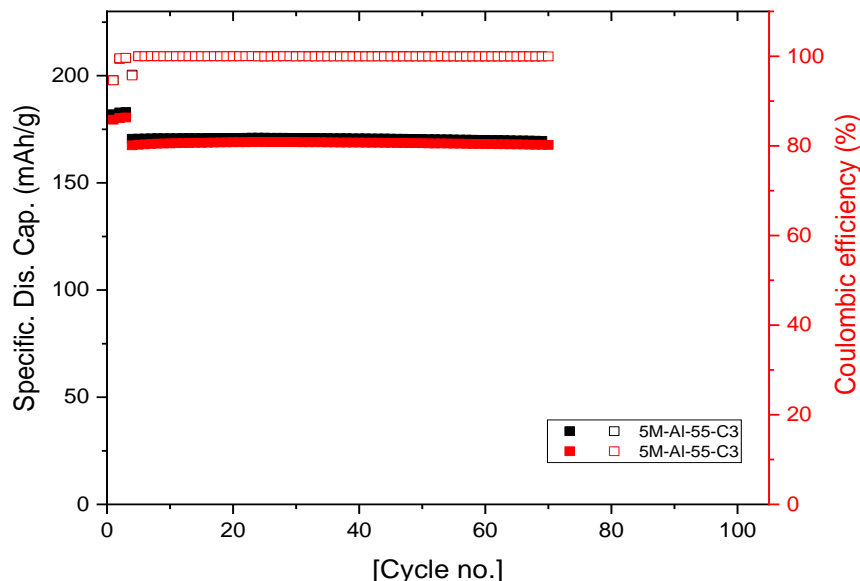
NMC532/Li half cell

4.3 – 3.0 V

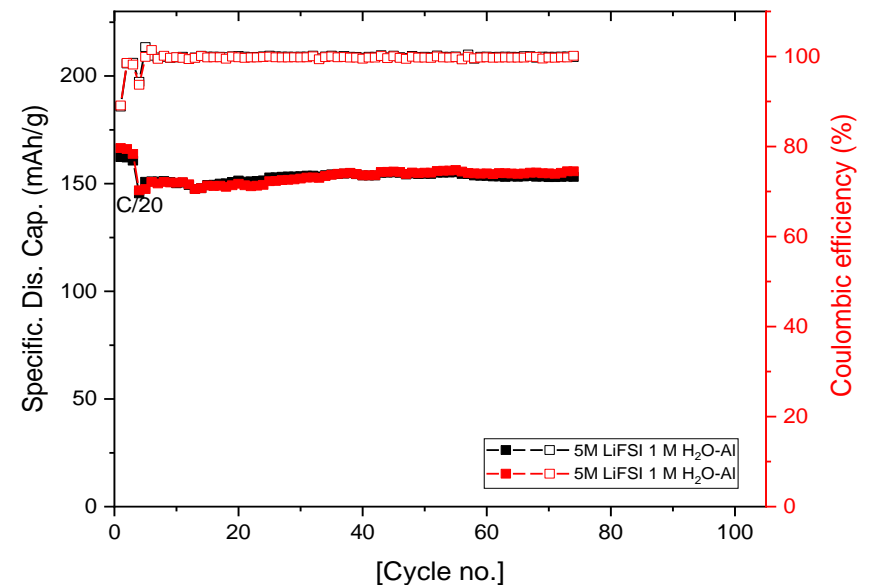
3 formation cycles @ C/20



$T = 55^{\circ}\text{C}$, C/3 cycling



H_2O added as diluent, C/3 cycling



- ✓ Increase the temperature will further enhance the conductivity of the electrolyte yielding a high C-rate.
- ✓ H_2O acts as a great choice of diluent for the high-concentration IL electrolytes, providing a facile Li^+ conducting channel.

Compatibility with Anode: NMC532/Si-Graphite Full Cell

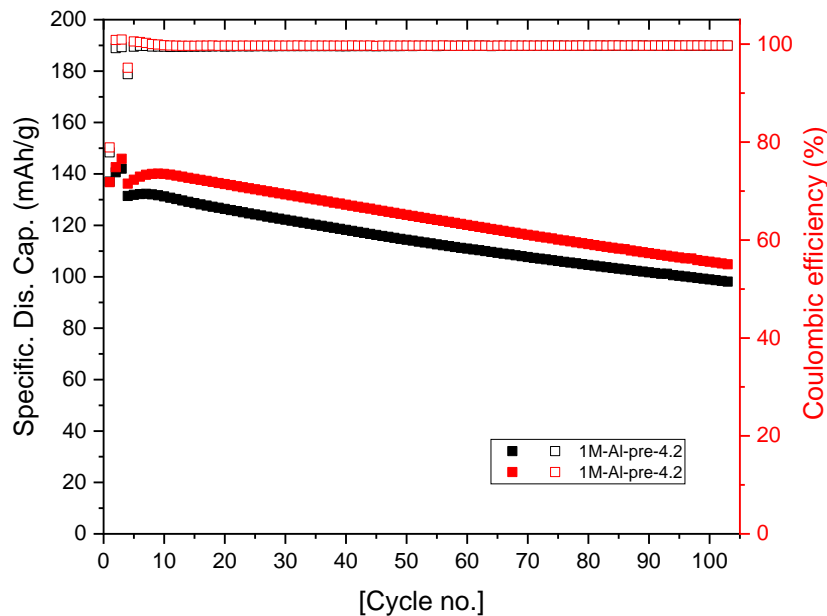
NMC532/Si-Graphite full cell

Cutoff Voltage: 4.2-3.0 V

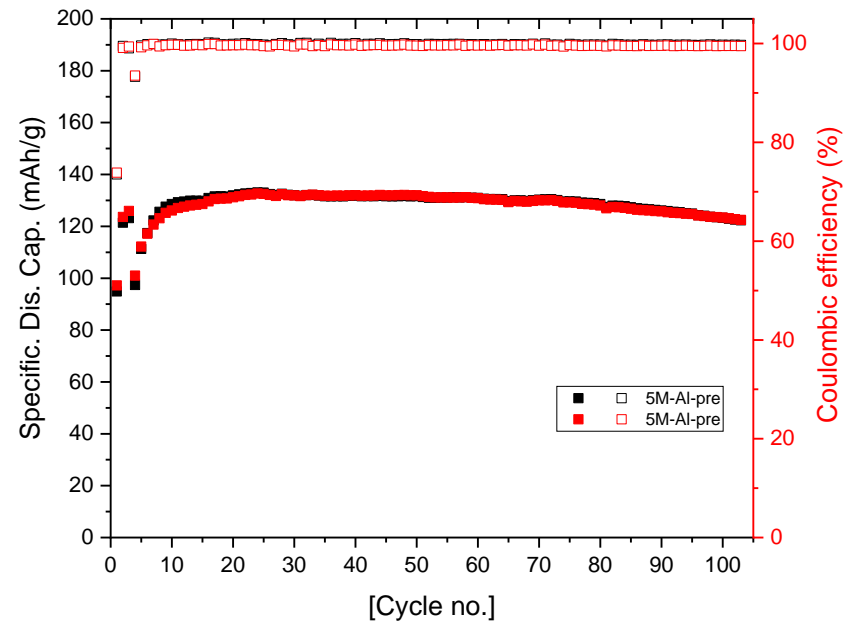
Current: C/10

Cycling T = 30°C

1 M LiFSI

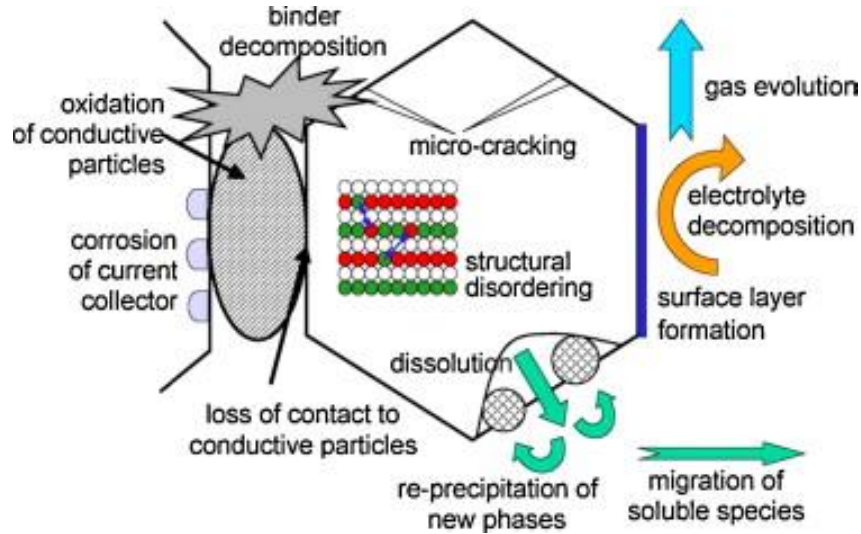


5 M LiFSI

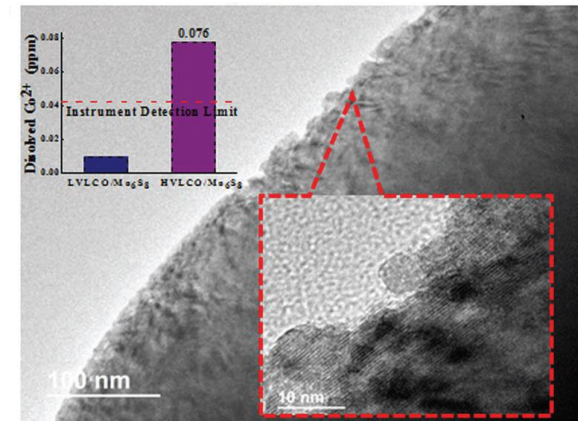
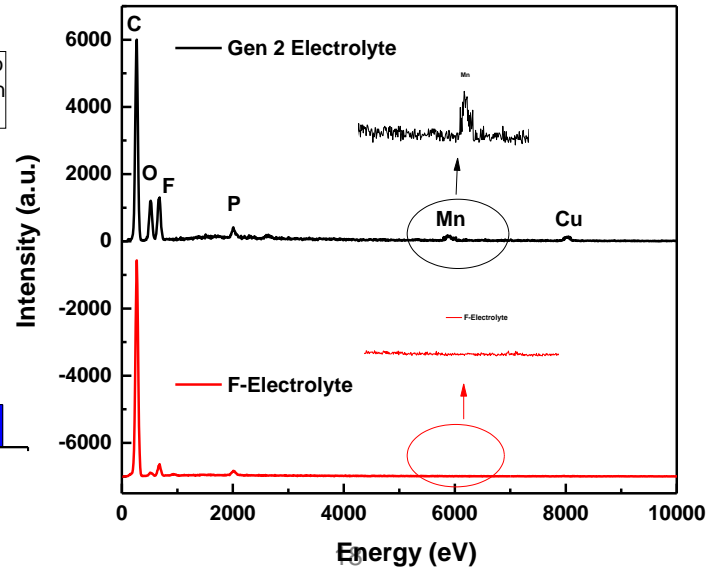
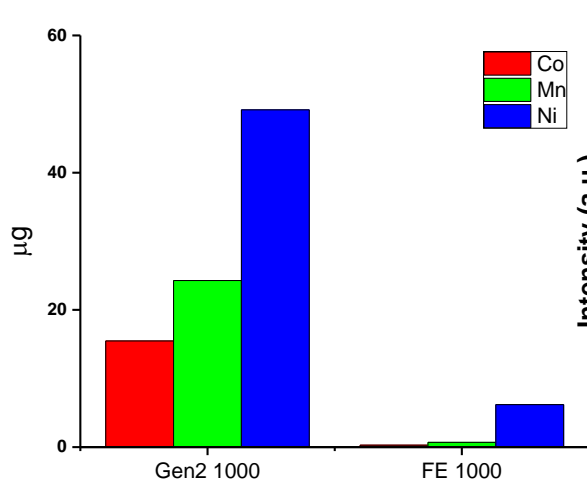


- ✓ Both 1 M and 5 M IL electrolyte cells show improved capacity retention compared with Gen 2 conventional electrolyte cell in NMC/Si-Gr full cell.
- ✓ It is manifest that 5 M high concentration full cell outperforms the 1 M low concentration one, indicating a different mechanism.

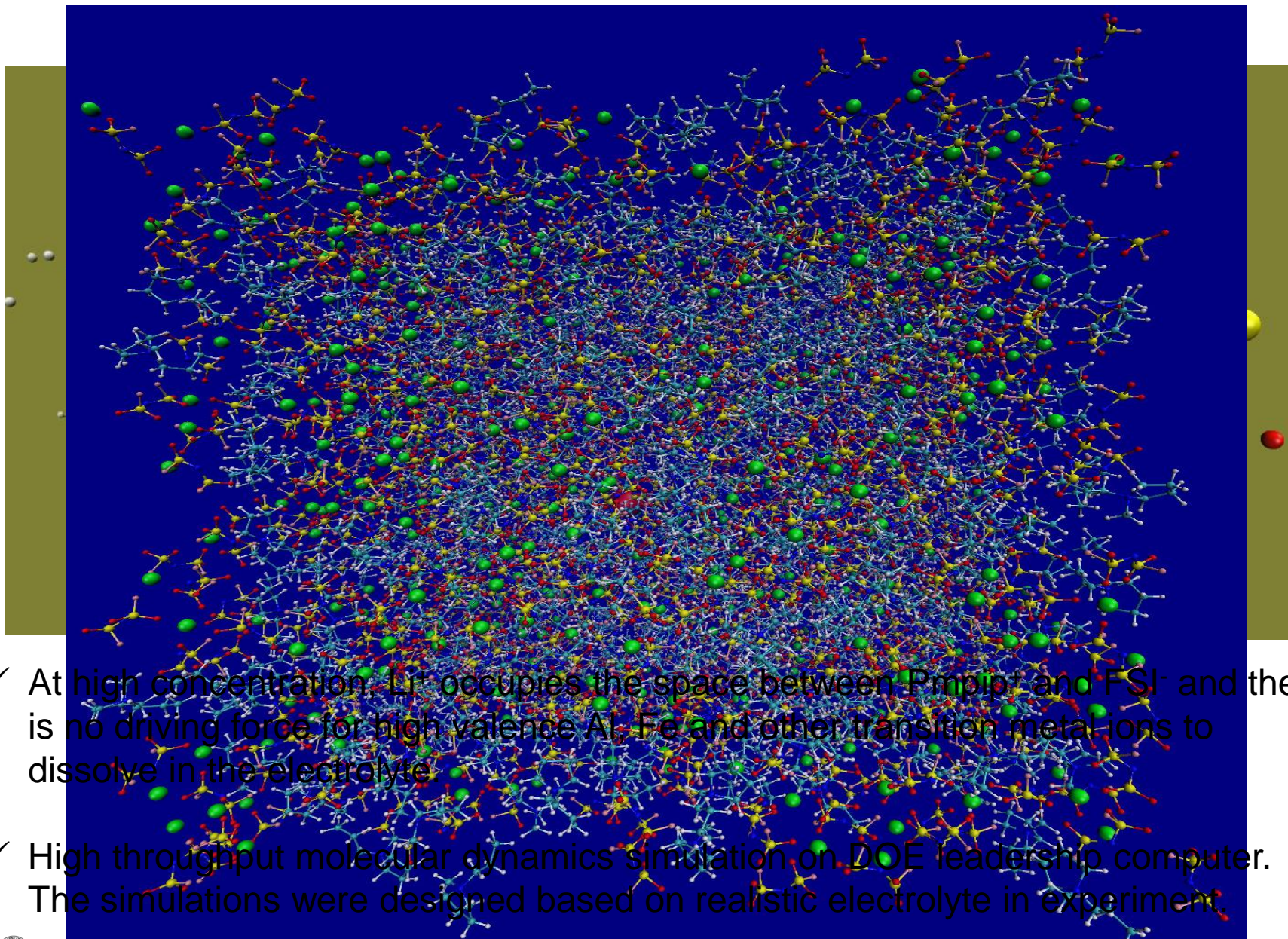
Degradation Mechanism of High-Voltage Li-ion Battery



J. Power Sources, 2005, 147, 269-281
Adv. Energy Mater., 2017, 7, 1700109
Nano Energy, 2019, 55, 216-225
Nano Lett., 2019, 19 (1), 29-37

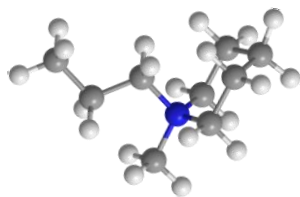


Snapshot from Molecular Dynamics Trajectory

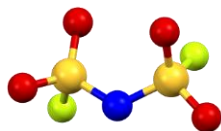


- ✓ At high concentration, Li^+ occupies the space between Pmpip^+ and F-SI^- and there is no driving force for high valence Al, Fe and other transition metal ions to dissolve in the electrolyte.
- ✓ High throughput molecular dynamics simulation on DOE leadership computer. The simulations were designed based on realistic electrolyte in experiment.

MD Simulation: Quantitative Structural Analysis



Pmpip⁺



FSI⁻

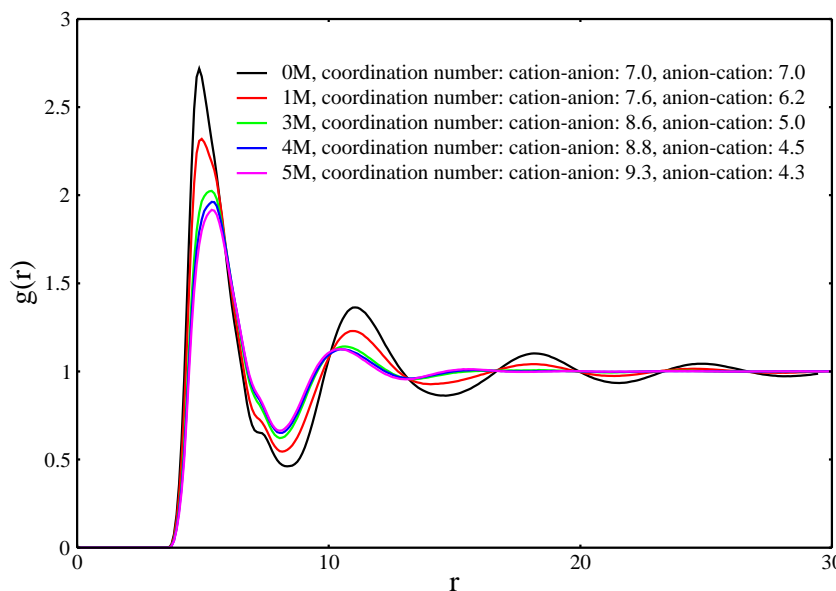


Li⁺

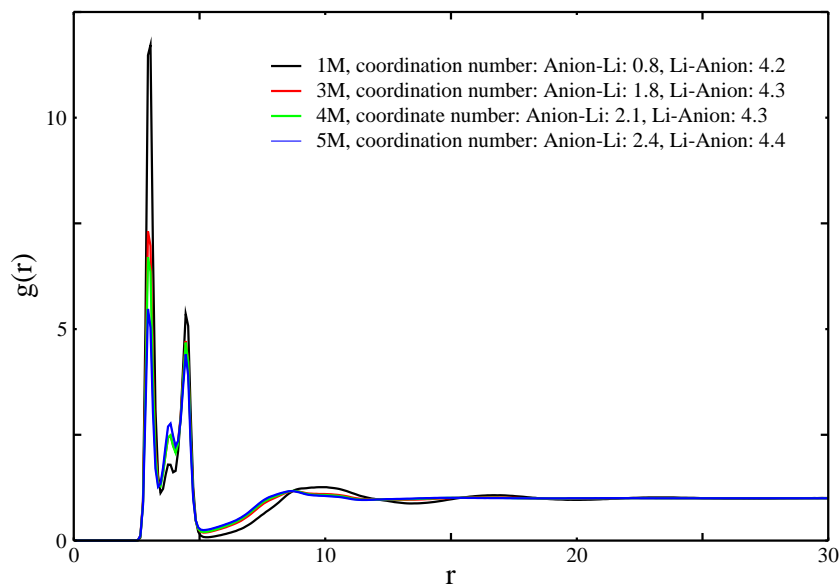


FSI⁻

Cation-Anion correlation



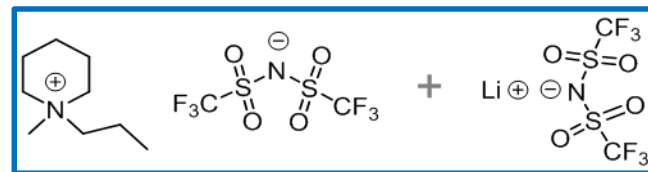
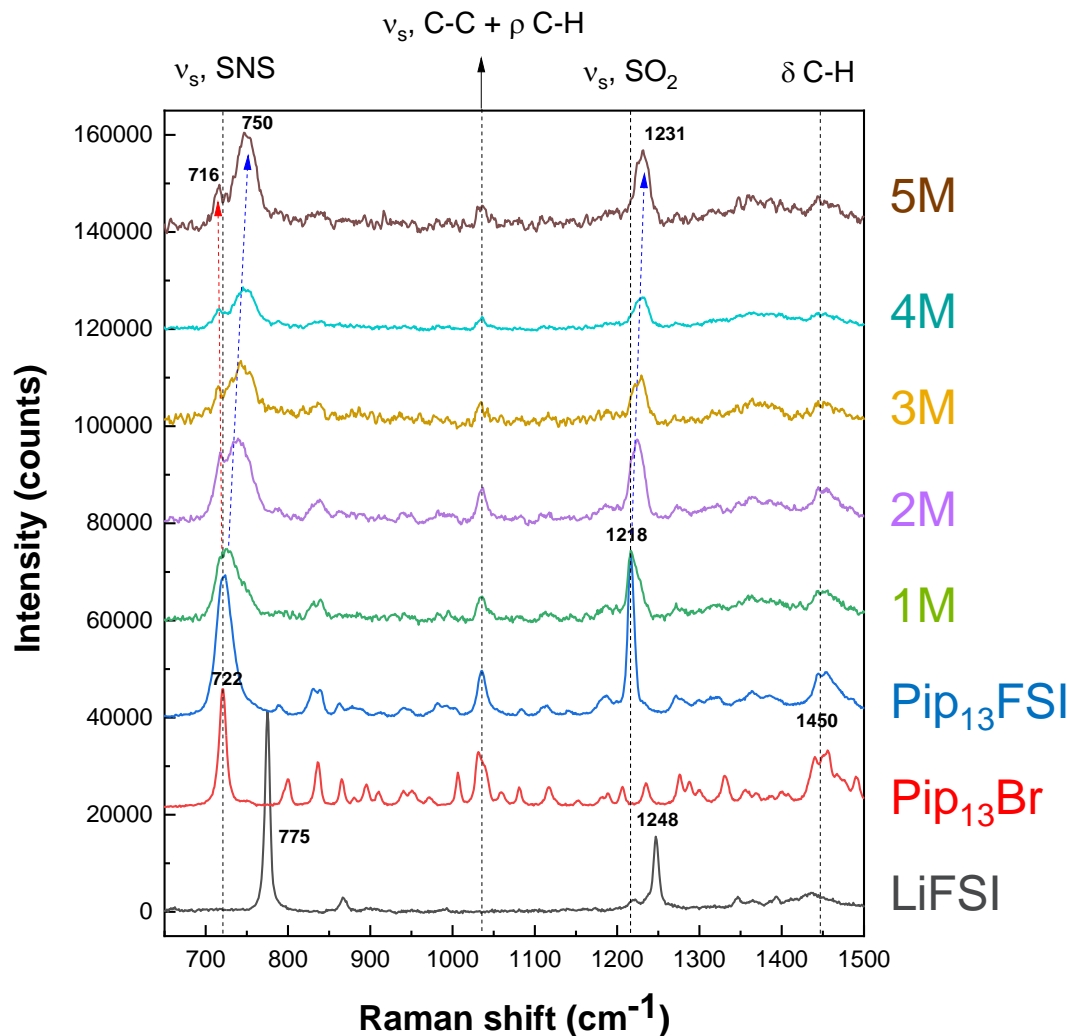
Anion-Lithium correlation



- ✓ The strong correlations of cation-anion and anion-lithium ion reveal highly ordered nanostructural organization, where lithium ions are distributed between solvation layers of cation-anion.

Spectroscopic Evidence: Raman Analysis

700 – 1500 cm^{-1} range



- ✓ $-\text{SNS}-$ and $-\text{SO}_2-$ vibrational peaks in FSI^- are shifted to lower wavenumbers in $\text{Pip}_{13}\text{FSI}$ than those in LiFSI salt
- ✓ Pip_{13}^+ has a band showing at the same wavenumber as FSI^-
- ✓ The main shifts are observed in the range of 700-1500 cm^{-1} when $[\text{LiFSI}]$ increases ($\geq 2 \text{ M}$).
- ✓ $\nu_{\text{s}, \text{SNS}}$ band of FSI^- is shifted to **higher wavenumber**, which is typical feature of **Li-coordinated** ion pairs or aggregated clusters. For 2 M solution, it showed at 740 cm^{-1} and further increased to 750 cm^{-1} for the 3-5 M solutions.
- ✓ $\nu_{\text{s}, \text{SO}_2}$ is also **blue-shifted** to 1226 cm^{-1} for 2 M solution and at 1231 cm^{-1} for 3-5 M solutions.

Response To Previous Year Reviewer's Comments

This project is a new start

Collaboration and Coordination with Other Institutions

Dr. Jason Croy – Argonne CSE, *Cathode materials*

Dr. Larry Curtiss – Argonne MSD, *DFT calculation*

Drs. Wei Jiang & Ying Li – Argonne Leadership Computing, *MD simulation*

Dr. Gregory Krumdick and Krzysztof Pupek – Argonne AMD, *Precursor scale-up*

Prof. Reza S. Yassar – University of Illinois - Chicago, *HR-TEM/EELS*

Prof. Tao Xu – Northern Illinois University, *Cathode surface protection*

Dr. Sheng S. Zhang, US Army Research Laboratory, *Cathode and Additive*

Dr. Peter de Wit – Lydall Performance Materials (Netherlands) - *Separator*



Remaining Challenges and Barriers

- ❑ Synthetic challenges for fully fluorinated compounds as potential high-voltage electrolyte solvents - fluorinated carbonates and fluorinated sulfones.
- ❑ Further enhance the Li^+ transport in super-concentrated ionic liquid-based electrolytes, and further improve the C-rate or power capability of the high voltage Li-ion batteries.
- ❑ SEI formation mechanism on graphite anode; tailor the formation of solid-electrolyte-interphase (SEI) on the graphite anode: low interfacial impedance and fast Li^+ transport kinetics.
- ❑ Molecular dynamics simulation Further improve the chemical/electrochemical stability at the Silicon/electrolyte interface to enable the high-voltage high-energy lithium-ion battery.

Proposed Future Research

- ✓ Optimization of *Ionic Liquid-Li Salt-Diluent* electrolyte systems for low viscosity, high Li⁺ transport and high C-rate and power capability.
- ✓ Molecular dynamics simulation for bulk properties of *Ionic Liquid-Li Salt-Diluent* electrolyte.
- ✓ Electrochemical evaluation of *Ionic Liquid-Li Salt-Diluent* electrolyte in high-voltage cathode half cells.
- ✓ Modeling the thermodynamics at cathode/electrolyte interphase at various delithiation stage (SOC) of Ni-rich low-cobalt cathode.
- ✓ Evaluation and modeling the SEI formation at anode/electrolyte interphase – both graphite and Si anode.
- ✓ Electrochemical evaluation of *Ionic Liquid-Li Salt-Diluent* electrolyte in high-voltage Li-ion full cells.
- ✓ Design and synthesis of new functionalized ILs with tailored properties and SEI formation capability.

Summary

A polyfluorinated carbonate electrolyte comprising 1.0 M LiPF_6 in difluoroethylene carbonate (DFEC)/bis(2,2,2-trifluoroethyl) carbonate (HFDEC) (3/7 in weight ratio) was demonstrated in a as a high-voltage enabling electrolyte was demonstrated in a $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ /graphite full cell.

The fluorinated electrolyte showed much improved Coulombic efficiency and capacity retention when a high cutoff voltage (4.5 V) was applied. The electrolyte suppresses the dissolution of TMs and is able to form a resilient SEI on the anode which mitigates the active lithium loss caused by the TM-catalyzed parasitic reactions.

High LiFSI concentration plays an important role in high voltage stability (up to 5 V), suppression of stainless steel corrosion, SEI formation capability on Si anode, high Li^+ transference number (t_{Li^+}) and high temperature stability.

Super-concentrated ionic liquid electrolytes based on PMpipFSI/LiFSI were studied as high voltage electrolyte and its advantage was demonstrated in NMC532/Li cycled at 4.5 V and 4.7 V and NMC532/Si-graphite full cells.

Molecular dynamics simulation reveals strong correlations of cation-anion and anion-lithium ion in the super-concentrated IL electrolyte, indicating a highly ordered nanostructural organization, where lithium ions are distributed between solvation layers of cation-anion.